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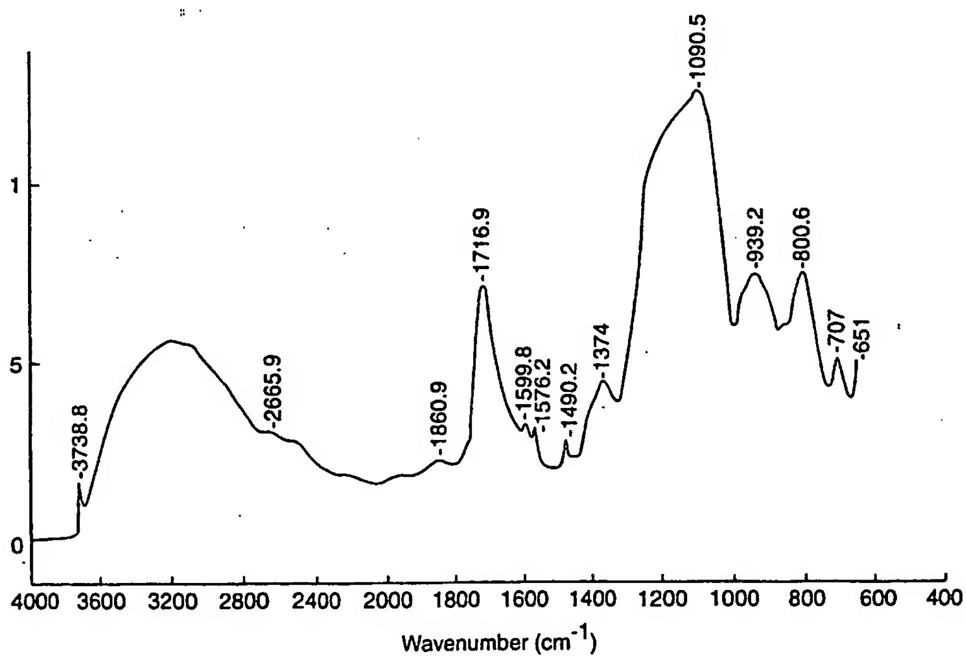
(54) Title: METAL ION FUNCTIONALIZED SILICA SURFACES FOR INK RECEPTORS



(57) Abstract: The invention provides ink receptor mediums that included organometallic multivalent metal salt on the silica surface of a silica-filled microporous substrate. The silica surface also may further include a surfactant and/or a binder.

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METAL ION FUNCTIONALIZED SILICA SURFACES FOR INK RECEPTORS

This invention relates to ink receptor media and, more particularly, to silica-filled microporous substrates having a coating that improves drying times of the ink, improves abrasion resistance of the image after drying, improves waterfastness of the printed image, and provides high quality images that are resistant to smudging and feathering.

Pigment fixation in a porous substrate is different than that in a non-porous substrate. In such microporous substrates as polypropylene membranes prepared using thermally induced phase separation techniques (that is, TIPS film) according to the disclosures of U.S. Patent Nos. 4,539,256 and 5,120,594, and EVAL (ethylene vinyl alcohol) film, available from Minnesota Mining and Manufacturing Company, St. Paul, MN, pigments are fixed at the sub-surface and sometimes within the wall of the capillaries in the bulk of the substrates. The fixation is usually carried out by metal ion flocculation of the pigmented ink at certain sheltered locations dictated by the flow and position of a surfactant or a combination of surfactants, migration inhibitor, and ink drying agent(s). This, in turn, is controlled by the type and nature of the surfactant(s) and other additives, as well as the pore size, size-distribution of the porous substrate(s) concerned.

In the case of TIPS film, for example, pigment flocculation is caused by a metal ion and flocculated or agglomerated pigmented ink is located at such a sheltered position, that is, in the bulk of the film where the surfactant and other additives are positioned, which is dictated by their flow. The chemical entanglement of the pigment is caused by the metal ion with the pigment dispersant but there is sufficient mechanical entanglement being provided by the pores due to pore-sizes. The entire process of pigment anchoring in porous films such as TIPS film is, in part, chemical. However, there are additional physical phenomena such as physical adsorption (physisorption) along the pores inside the pore-interconnected bulk of the film. The optical density of the imaged film usually is somewhat lower than in the case where all the pigmented ink could be laid down on top of the surface.

Substrates with very limited pore sizes may allow only water percolation retaining the pigment onto the surface level. This is the situation with the surface of TESLIN brand

film, available from PPG Industries, Pittsburgh, PA. TESLIN film is a silica-filled high density polyethylene substrate having very small pore sizes (typically 0.02-0.5 micrometers). When TESLIN film is imaged with pigmented ink, the pigment remains on the surface and does not penetrate below the surface into the pores for sheltering at the sub-surface level. Such a substrate provides very high optical density and high quality images, but such images are not water-fast.

In one embodiment, the invention provides an ink receptor medium comprising a silica-filled microporous substrate having a silica surface and an organometallic multivalent metal salt on the silica surface of the silica-filled microporous substrate. The ink receptor media of the invention may also further comprise a surfactant, a binder, or a combination of surfactant and binder on the surface of the silica-filled microporous substrate. The surfactant is preferably hydrophilic. The surface of the silica-filled microporous substrate may be partially or substantially fully covered with the organometallic multivalent salt.

The novel ink receiving media when imaged using an inkjet printer provide durable, high color intensity and high quality images which are tack-free and rapidly dry to the touch.

In another embodiment, the invention provides an imaged ink receptor medium comprising a silica-filled microporous substrate having a silica surface and an organometallic multivalent metal salt on the silica surface of the silica-filled microporous substrate and ink on the surface of silica-filled microporous substrate and in contact with the organometallic multivalent metal salt. In a preferred embodiment, the ink colorant is a pigment dispersion having a dispersant bound to the pigment that will destabilize, flocculate, agglomerate, or coagulate on contact with the ink receiving medium. Preferably, the image is made using an ink jet printer head.

In another embodiment, the invention provides an ink receptor medium intermediate comprising an aqueous composition comprising an organometallic salt on a silica surface of a silica-filled microporous substrate.

The present invention also provides an ink receiving medium/ink set comprising a silica-filled microporous substrate having a silica surface and an organometallic multivalent metal salt on the silica surface of the silica-filled microporous substrate, and an ink that contains pigment colorants.

The ink receptor media of the invention provides silica-filled microporous substrates that are water and abrasion resistant (that is, substantially wash-fast) by chemically modifying the silica surface of the silica-filled substrate. Additionally, the ink receptor media of the invention provide higher color density and sharper images than those of the non-porous silica-filled substrates.

An advantage of ink receiving media of the present invention is that a laminated protective cover layer is not necessary to achieve water resistant images.

Other features of ink receiving media of the invention include that they: work with pigmented inks, have high resolution, have high color density, provide wide color gamut, are waterfast, are smudge resistant, and provide rapid drying.

Figure 1 is an infrared spectrum of silica particles modified by multifunctional organic acid.

The microporous substrates useful in the invention are so called "silica-filled" microporous substrates. "Silica-filled" substrates are substrates that are filled with silica particles. These substrates are typically made by impregnation of silica particles into the polymer matrix. The process involves co-extrusion of both the polymer and the silica at appropriate processing temperature and pressure as well as axial orientation to induce pores into the resulting film. Typically, these substrates have very small pore sizes on the order of 0.02 to 0.5 micrometers and may be prepared according to methods described in one or more of U.S. Patent Nos. 4,833,172; 4,861,644; 4,877,679; and 4,892,779.

The silica present on the surface of the microporous substrates is amorphous silica. Amorphous silica usually consists of a silicon dioxide wherein the silicon atom is tetrahedrally bound to the oxygen atoms bridged between the silicon atoms. In an aqueous environment, a certain percentage of silanol groups exist on the silica surface. Under acidic conditions, this percentage is increased. In the present invention, for example, the Al^{+3} ion and the –COOH functionality are believed to react with the Si-OH group to give -Al-O-Si- and -C(=O)-O-Si- linkages which are surface-bound. Evidence for the surface interactions has been shown by infrared spectroscopy. Infrared spectroscopy for aluminosilicates (for example, Kaolinite, Kaolin, feldspar, etc.) show characteristic absorption bands at 680-1100 cm-1. (See Sadtler Research Lab, Division of Bio-Rad Lab, Spectrum Nos. 354, 355). The IR spectrum of silica particles modified by multifunctional organic acids (such as sulfocarboxylic acid) according to the present invention has a

similar absorption band accompanied by a carbonyl absorption band at ~1715 cm-1 as shown in Figure 1.

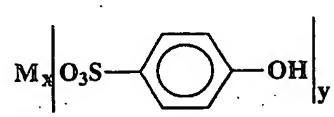
While wishing not to be bound by theory, it is believed that pigmented inks are flocculated, that is, the pigment is removed from the dispersion, by binding to surface bound $M^{+(3-n)}$ ions.

Pigment usually rests on the dispersion(s) used in the preparation and composition of the pigmented based ink(s).' For the anionic dispersant(s), the anions, for example, a carboxylate anion, instantaneously react with the surface-bound aluminum cation leading to coagulation/flocculation of the ink. The ink, thus, is also surface-bound and is not prone to hydrolysis (no wash-away). The product materials on the silica surface, aluminum carboxylates, and aluminum silicates are usually insoluble end-products.

Preferred silica-filled substrates are commercially available from PPG Industries, Pittsburgh, PA, having the tradename TESLIN, and from Texwipe, Saddle River, NJ, under the tradename TEXWRITE (for example TEXWRITE MP10).

Useful organometallic salts are those which have a multivalent metal ion and a multifunctional organic acid anion or counterion. Examples of the multivalent metal ions include, but are not limited, Al, Ga, Ti, Zr, Hf, Zn, Mg, Ca, Nb, Ta, Fe, Cu, Sn, Co, and the like. Examples of the organic acid include, but are not limited to, aromatic dicarboxylic, tri-, tetra- and penta-carboxylic, sulfocarboxylic, di-, tri-, tetra-sulfocarboxylic, and any combination thereof, hydroxycarboxylic, hydroxysulfonic, hydroxysulfocarboxylic, and any combination in number thereof in any aromatic system.

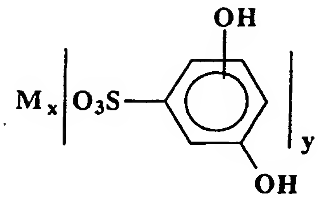
Specific examples of useful organometallic salts include metal sulfocarbolates having the formula:



wherein

when M is Cu, Mg, Zn, Ca, or Co, the ratio of x:y is 1:2; and when M is Al, Ga, B, then the ratio of x:y is 1:3 or 2:3;

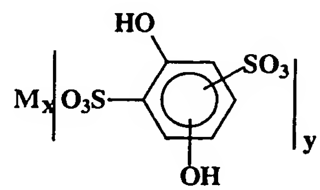
metal hydroquinonesulfonates having the formula:



wherein

when M is Cu, Mg, Zn, Ca, or Co, the ratio of x:y is 1:2 or 2:2; and when M is Al, Ga, B, Ti, Zr, or Hf, the ratio of x:y is 1:3, 2:3 or 2:2;

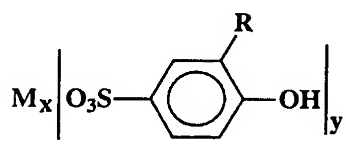
metal dihydroxybenzenedisulfonates having the formula:



wherein

when M is Cu, Mg, Zn, Ca, or Co, the ratio of x:y is 1:2 or 2:2; and when M is Al, Ga, B, Ti, Zr, or Hf, the ratio of x:y is 1:1, 1:3, 2:2, or 4:3;

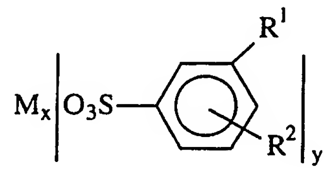
metal sulfosalicylates having the formula:



wherein

when M is Cu, Mg, Zn, Ca, or Co, the ratio of x:y is 1:2 or 1:1; when M is Al, Ga, B, Ti, Zr, or Hf, the ratio of x:y is 1:3, 2:3, or 3:3; and R is –COOH (Li, Na, or K);

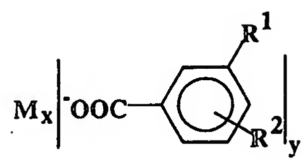
metal sulfophthalates having the formula:



wherein

when M is Cu, Mg, Zn, Ca, or Co, the ratio of x:y is 3:2, 2:2 or 1:1; when M is Al, Ga, B, Ti, Zr, or Hf, the ratio of x:y is 1:3, 2:2, or 2:3; R1 is H or –COOH (Li, Na, or K); and R2 is –COOH (Li, Na, or K); and

metal carboxylates having the formula:



wherein

when M is Cu, Mg, Zn, Ca or Co, then the ratio of x:y is 1:1, 2:2, or 3:2; when M is Al, Ga, B, Ti, Zr, or Hf, then the ratio of x:y is 1:3, 2:2, or 2:3; R1 is H or COOH (Li, Na, or K) and R2 is COOH ((Li, Na, or K).

Specific examples of preferred organometallic multivalent metal salts include magnesium sulfophthalate, copper sulfophthalate, zirconium sulfophthalate, zirconium phthalate, aluminum sulfophthalate, aluminum sulfoisophthalate, and combinations thereof.

The surfaces of the silica-filled microporous substrates of the invention may also further optionally comprise surfactant, binder, or a combination thereof. Sometimes, the chemical and physical properties (for example, surface energy) of the microporous surface requires assistance from surfactants to aid in the management of ink fluids. Therefore, at least one surfactant may be advantageously impregnated into the pore volume of the microporous substrate. Application of the surfactant may be performed as a separate and distinct step, or combined with the organometallic salt and coated onto the substrate in a single step, followed by removal of any water and/or organic solvent or solvents, to provide particularly suitable surfaces for the particular fluid components of the pigmented inkjet inks.

Surfactants can be cationic, anionic, nonionic, or zwitterionic. Many of each type of surfactant are widely available to one skilled in the art. Accordingly, any surfactant or

combination of surfactants or less preferably, polymer(s) that will render said substrate hydrophilic, could be employed.

These may include but are not limited to fluorochemical, silicone, and hydrocarbon-based surfactants wherein the said surfactants may be anionic or non-ionic. Furthermore, the non-ionic surfactant may be used either as it is or in combination with another anionic surfactant in water and/or organic solvent or solvents, said organic solvent being selected from the group consisting of alcohols, ethers, amides, ketones, and the like.

Various types of non-ionic surfactants can be used, including but not limited to: ZONYL fluorocarbons, for example, ZONYL FSO, available from E.I. du Pont de Nemours and Co., Wilmington, DE; FLUORAD FC- 170 or 171 surfactants, available from Minnesota Mining and Manufacturing Company; PLURONIC block copolymers of ethylene and propylene oxide to an ethylene glycol base, available from BASF Corp. Chemicals Division, Mount Olive, NJ; TWEEN polyoxyethylene sorbitan fatty acid esters, available from ICI Americas, Inc., Wilmington, DE; TRITON X series octylphenoxy polyethoxy ethanol, available from Rohm and Haas Co., Philadelphia, PA; SURFYNOL tetramethyl decynediol, available from Air Products and Chemicals, Inc., Allentown, PA; and SILWET L-7614 and L-7607 silicon surfactants, available from Union Carbide Corp., Danbury, CT, and the like known to those skilled in the art.

Useful anionic surfactants include, but are not limited to, alkali metal and (alkyl)ammonium salts of: 1) alkyl sulfates and sulfonates such as sodium dodecyl sulfate and potassium dodecanesulfonate; 2) sulfates of polyethoxylated derivatives of straight or branched chain aliphatic alcohols and carboxylic acids; 3) alkylbenzene or alkylnaphthalene sulfonates and sulfates such as sodium laurylbenzene-sulfonate; 4) ethoxylated and polyethoxylated alkyl and aralkyl alcohol carboxylates; 5) glycinates such as alkyl sarcosinates and alkyl glycinates; 6) sulfosuccinates including dialkyl sulfosuccinates; 7) isethionate derivatives; 8) N-acyltaurine derivatives such as sodium N-methyl-N-oleyltaurate); 9) amphoteric alkyl carboxylates such as amphoteric propionates and alkyl and aryl betaines, optionally substituted with oxygen, nitrogen and/or sulfur atoms; and 10) alkyl phosphate mono or di-esters such as ethoxylated dodecyl alcohol phosphate ester, sodium salt.

Useful cationic surfactants include alkylammonium salts having the formula $C_nH_{2n+1}N(CH_3)_3X$, where X is OH, Cl, Br, HSO_4 or a combination of OH and Cl, and

where n is an integer from 8 to 22, and the formula $C_nH_{2n+1}N(C_2H_5)_3X$, where n is an integer from 12 to 18; gemini surfactants, for example those having the formula: $[C_{16}H_{33}N(CH_3)_2C_mH_{2m+1}]X$, wherein m is an integer from 2 to 12 and X is as defined above; aralkylammonium salts such as, for example, benzalkonium salts; and cetylethylpiperidinium salts, for example, $C_{16}H_{33}N(C_2H_5)(C_5H_{10})X$, wherein X is as defined above.

The amount of organometallic multivalent salt that can be used in the intermediate for imbibing in the microporous substrate of the present invention can range from 0.1 weight percent to 50 weight percent, and preferably from 0.5 weight percent to 20 weight percent.

The amount of surfactant that can be used in the intermediate for imbibing in the microporous substrate of the present invention can range from 0.01 weight percent to 10 weight percent, and preferably from 0.1 weight percent to 5 weight percent.

Optionally, organic binders can be used in the ink receiving media of the invention. Preferably, the organic binders are soluble or dispersible in water so that they may be easily incorporated into the intermediate compositions used to coat microporous substrates in forming the ink receiving media of the invention. Non-limiting examples of such organic binders include acrylic emulsions, styrene-acrylic emulsions, polyvinyl alcohol, polyvinyl alcohol/acrylic acid combinations, and combinations thereof, and the like. Such organic binders can be present in the coating or intermediate solution from 0.1 to 50 weight percent, preferably 1 to 30 weight percent based on total weight of the coating or intermediate solution, including surfactants and metal salts, with the remainder being water and/or organic solvent.

Optionally, opacifying pigments can be used in ink receiving media of the present invention. Non-limiting examples of such opacifying pigments include titanium dioxide pigments, barium sulfate pigments, and the like. Such opacifying pigments can be present in the coating solution and can range from 0.01 weight percent to 50 weight percent. Preferably, the opacifying pigment is present in an amount from 1 to 30 weight percent.

Optionally, heat or ultraviolet light stabilizers can be used in ink receptors of the present invention. Non-limiting examples of such additives include TINUVIN 123 or 622LD, or CHIMASSORB 944 (hindered amine light stabilizers), available from Ciba Specialty Chemicals Corp., Tarrytown, NY); and UVINUL 3008, available from BASF

Corporation Chemicals Division. Such stabilizers can be present in a coating or intermediate solution to be impregnated into the microporous substrate in the range from 0.2 weight percent to 20 weight percent. Preferably, the stabilizer is present in an amount from 0.1 to 10 weight percent, more preferably in an amount of from 0.5 to 5 weight percent.

Optionally, ultraviolet light absorbers can be used in ink receiving media of the present invention. Non-limiting examples of such absorbers include TINUVIN II 30 or 326, available from Ciba Specialty Chemicals Corp.; UVINUL 40501 1, available from BASF Corporation, and SANDUVOR VSU or 3035, available from Sandoz Chemicals, Charlotte, NC. Such absorbers can be present in the coating or intermediate solution and can range from 0.01 weight percent to 20 weight percent. Preferably, the absorber is present in an amount from 1 to 10 weight percent.

Optionally, anti-oxidants can be used in ink receiving media of the present invention. Non-limiting examples of such anti-oxidants include IRGANOX 1010 or 1076, available from Ciba Specialty Chemicals Corp.; and UVINUL 2003 AD, available from BASF Corporation Chemicals Division.

Such anti-oxidants can be present in the coating or intermediate solution and can range from 0.2 weight percent to 20 weight percent. Preferably, the anti-oxidant is present in an amount from 0.4 to 10 weight percent, and more preferably in an amount from 0.5 to 5 weight percent.

An ink receiving medium of the present invention has two major opposing surfaces and can be employed for printing (for example, by inkjet methods) on both surfaces. Optionally, one of the major surfaces can be dedicated for the purpose of adhering the finished image graphic to a supporting surface such as a wall, a floor, or a ceiling of a building, a sidewall of a truck, a billboard, or any other location where an excellent quality image graphic can be displayed for education, entertainment, or information.

Minnesota Mining and Manufacturing Company offers a variety of image graphic receptor media and has developed an array of pressure-sensitive adhesive formulations that can be employed on the major surface opposing the surface intended for imaging. Among these adhesives are those disclosed in U.S. Patent Nos. 5,141,790 (Calhoun et al.); 5,229,207 (Paquette et al.); 5,800,919 (Peacock et al.); 5,296,277 (Wilson et al.); 5,362,516 (Wilson et al.); EPO Patent Publication EP 0 570 515 B1 (Steelman et al.), and

PCT Patent Application Nos. WO 97/31076 (Peloquin et al.) and WO 98/29516 (Sher et al.).

Any of these adhesive surfaces should be protected by a release or storage liner such as those commercially available from Rexam Release, Bedford Park, IL. Alternatively to adhesives, mechanical fasteners can be used if laminated in some known manner to that opposing major surface of the receptor of the present invention. Non-limiting examples of mechanical fasteners include hook and loop, Velcro™, Scotchmate™, and Dual Lock™ fastening systems, as disclosed in published PCT Patent Application No. WO 98/39759 (Loncar).

The invention in its preferred mode is made by impregnation of the microporous substrate with organometallic salt and with a suitable surfactant as required followed by drying at a temperature of 100 to 120 °C. After the receptor is dried, it can be imaged using conventional inkjet imaging techniques embodied in commercially available printers.

Impregnation of the organometallic multivalent salt may be accomplished by dissolving or mixing the salt or salt and surfactant in de-ionized water or a mixture of an alcohol and de-ionized water. Impregnation of the solution may be done using conventional equipment and techniques such as slot fed knife, rotogravure devices, padding operations, dipping, spraying, and the like. It is preferred that the organometallic multivalent metal salt fills the pores of the substrate without leaving substantial quantities on the surface. Excessive amounts of solids could plug the pores and in turn causes smearing and slow dry times during imaging. Coating weights depend on porosity, thickness, and chemical nature of the substrate, but may be readily determined by routine optimization. Typical wet coating weights are from 1 up to 500 grams per square meter, preferably from 10 up to 50 grams per square meter, more preferably from 15 to 30 grams per square meter. Optional additives may be added before, during, or after impregnation of the ink receptor intermediate.

The printing industry has previously employed dye-based inks, although pigment-based inks are becoming more prevalent. Use of pigment colorants is preferred over dye colorants because of durability and ultraviolet light stability in outdoor applications.

Further, reference to ink with respect to this invention concerns aqueous-based inks, not solvent-based inks. Aqueous-based inks are currently preferred in the printing

industry for environmental and health reasons, among other reasons.

Minnesota Mining and Manufacturing Company produces a number of excellent pigmented inkjet inks for thermal inkjet printers. Among these products are Series 8551, 8552, 8553, and 8554 pigmented inkjet inks. The use of four principal colors: cyan, magenta, yellow, and black permit the formation of as many as 256 colors or more in the digital image. Further, pigmented inkjet inks, and components for them, are also produced by others, including Hewlett-Packard Corp., Palo Alto, CA and E.I. du Pont de Nemours and Co., and a number of other companies that can be located at many commercial trade shows dedicated to the imaging and signage industries.

The metal-ion functionalized silica surfaces of the present invention are capable of capturing and flocculating or coagulating pigmented inks or colorants and thus fixing the colorants onto the silica surfaces. This property makes the metal-ion functionalized silica surfaces of the invention particularly suitable for use as an ink receptor.

Examples

In the following examples, the term "parts" means parts by weight, unless otherwise specified.

The HP Designjet 2500cp thermal inkjet printer, available from Hewlett-Packard Corp, was used with manufacturer's recommended inks (Part Nos. C1806A, C1807A, C1808A, C1809A). It is believed that the above black, yellow, magenta, and cyan inks are pigment based.

The exact nature of the image printed in the examples below is not critical in order to be able to reproduce the result obtained therein. The image employed was standard test patterns (for example CCL, circle tests, photographic images, etc.)

Wash-fastness Test

Printed films were evaluated for wash-fastness by placing them under a fully open running utility sink water faucet (25-30 °C). The wet imaged film was wiped with a paper towel until dry. If no discernible smearing or reduction of color density occurred, then the wash-fastness test was passed. Percentage color density loss was measured using a GRETAG M50 REFLECTANCE SPECTROPHOTOMETER, available from Gretag-Macbeth, Gastonia, NC, unless otherwise noted.

Example 1

Composition-I was flood-coated onto the surface of a silica-filled film (CHANGEABLE OPAGUE IMAGING MEDIA 8522CP), available from Minnesota Mining and Manufacturing Company, using a #4 Meyer Rod, available from RD Specialties, Webster, NY, to produce a nominal wet coating thickness of 0.0091 mm. The coated substrate was dried at 120-130 °C for 1-2 minutes to provide an ink receptor medium. When imaged using HP Designjet 2500cp thermal inkjet printers, a very high density, high quality, instantaneously dry image was obtained. The image was resistant to smudging with fingers, had good edge definition (without noticeable feathering), and visually passed the wash-fastness test.

Composition-I

Ingredients	Parts
Aluminum(III) Sulfophthalate (Organometallic Salt)	10
Dihexylsulfosuccinate-Na Salt (Surfactant)	6
Poly vinylpyrrolidone/Acrylic Acid) (PVP/AA) (75:25) (Binder)	2
Isopropyl Alcohol	25
De-ionized Water	57

Example 2

A 24 inch x 16 inch (61 x 41 cm) TESLIN film substrate was flood coated with Composition-I over one-half of its surface (as described in Example 1) and the remaining half of the surface was left uncoated. The coated substrate was dried as described above to form an ink receptor medium. The dry substrate was imaged using a HP Designjet-2500cp thermal inkjet printer to obtain a very high color density image as described above. The image on the coated portion of the image provided a higher density image than did the un-coated surface. The imaged substrate was laminated onto an aluminum board/backing (poster board) and subjected to the wash-fastness test. The image on the un-coated TESLIN film substrate washed away. The image fading was very pronounced and easily observed by the naked eye. The image on the coated TESLIN film surface (the present invention) passed the wash-fastness test with insignificant loss (about 1 percent) of color.

Example 3

The procedure of Example 2 was repeated except that the dihexylsulfosuccinate-Na salt of Composition-I was eliminated and replaced with an equivalent amount of

deionized water. The image on the coated substrate was a very high density image that was smudge-free and free of feathering, except about 5-10 percent of the colors black and green were lost during the wash-fastness test.

Example 4

The procedure of Example 2 was repeated except that the PVP/AA binder was eliminated from Composition-I and replaced with an equivalent amount of deionized water. The image on the coated substrate was a very high density image that was smudge-free and free of feathering, except that the color black appeared to be more on top of the surface and about 5-10 percent of the colors black and green was lost in the wash-fastness test.

Example 5

The procedure of Example 2 was repeated except that both the PVP/AA binder and dihexylsulfosuccinate-Na salt were eliminated from Composition-I and replaced with an equivalent amount of deionized water. The image on the coated substrate was a very high density image that was smudge-free and free of feathering, except that the color black appeared to be more on top of the surface and there was some pigment beading and coalescence together with some minor banding. In the wash-fastness test, about 5-10 percent of the colors black and green were lost.

Example 6

The procedure of Example 2 was repeated except that bis-aluminum (III) sulfophthalate was substituted for aluminum(III)sulfophthalate in Composition-I. The effect was an increase in the amount of aluminum ions in the composition. The image on the coated substrate was a very high density image that was smudge-free and free of feathering. However, the image was slightly less dry after printing than the image of Example 2 and in the wash-fastness test, about 5-10 percent of the colors red and green color was lost.

Example 7

The procedure of Example 2 was repeated except that tris-aluminum (III) sulfophthalate was substituted for aluminum(III) sulfophthalate in Composition-I. The effect was an increase in the amount of aluminum ions in the composition. The image on the coated substrate showed ink beading, coalescence, feathering, smudginess and the image was not dry after printing. In the wash-fastness test, about 30-40 percent of the colors red and green were lost.

Example 8

Composition-II was flood-coated onto a surface of a silica-filled substrate as described in Example 1 to provide a nominal wet coating thickness of about 0.0091 mm. The coated film was dried as in Example 1 to form an ink receptor medium. When imaged using an HP Designjet 2500cp thermal inkjet printer, the ink receptor medium provided a very high density, high quality, instantaneously dry image. The image was smudge-free, feathering-free; and substantially passed the wash-fastness test.

In Examples 1-8, the image on the uncoated part of the substrate washed away in the wash-fastness test (failed).

Composition-II

Ingredient	Parts
Zirconium Tetrakis(Sulfophthalate) (Organometallic Salt)	9
Dihexylsulfosuccinate-Na Salt (Surfactant)	6
Isopropyl Alcohol	25
De-ionized Water	58

Example 9

A 24 inch x 16 inch (61 x 41 cm) piece TESLIN film was flood coated with Composition-II over one-half of its surface (as described in Example 1) and the remaining half of the surface was left uncoated. The coated substrate was dried as described above to form an ink receptor medium. The dry substrate was imaged using an HP Designjet thermal inkjet to obtain a very high density image as described above. The image on the coated portion of the image provided a higher density image than did the un-coated surface. The imaged substrate was laminated onto an aluminum board/backing (poster board). The image was then subjected to the wash-fastness test. Ninety-percent of the image on the un-coated surface was washed away. The image on the coated portion of the image (the invention) survived with insignificant loss (about 3-5 percent) of color.

Example 10

The procedure of Example 9 was repeated except that titanium tetrakis(sulfophthalate) was substituted for zirconium tetrakis(sulfophthalate). The printed image had similar image quality to that of the image of Example 9. The image on the uncoated part of the substrate washed away and about 10-20 percent of the image on the coated part of the substrate was washed away after the wash-fastness test.

Example 11

The procedure of Example 9 was repeated except that copper(II) sulfosalicylate was substituted for zirconium tetrakis(sulfophthalate). The printed image had similar image quality to that of the image of Example 9. The image on the uncoated part of the substrate washed away and about 5-10 percent of the image on the coated part of the substrate was washed away after the wash-fastness test.

Example 12

Composition-III was flood-coated onto a CHANGEABLE OPAQUE IMAGING MEDIA 8522CP film to form a nominal wet coating thickness of 0.0091 mm and then dried as described in Example 1 to form an ink receptor medium. When the ink receptor medium was imaged using an HP Designjet 2500cp thermal inkjet printer, the ink receptor medium provided a very high density, high quality, instantaneously dry image that was also smudge-free, feathering-free, and passed the wash-fastness test.

Composition-III

Ingredients	Parts
Magnesium Sulfophthalate (Organometallic Salt)	10
Dihexylsulfosuccinate-Na Salt (Surfactant)	6
PVP/AA (75:25) (Binder)	2
Isopropyl Alcohol	25
De-ionized Water	57

Example 13

A 24 inch x 16 inch (61 x 41 cm) piece of TESLIN film was flood coated with Composition-III over one-half of its surface (as described in Example 1) and the remaining half of the surface was left uncoated. The coated substrate was dried as described above to form an ink receptor medium. The dry substrate was imaged using an HP Designjet 2500cp thermal inkjet printer to obtain a very high density image as described above. The image on the coated portion of the image had a higher density image than did the un-coated surface. The imaged substrate was laminated onto an aluminum board/backing (poster board). The image was then subjected to the wash-fastness test. Ninety-percent of the image on the un-coated surface was washed away. The image on the coated portion of the surface (the invention) survived with a small loss (about 10-15 percent) of color, and substantially passed the wash-fastness test.

Example 14

Composition-IV was flood-coated onto a TESLIN film to form a nominal wet coating thickness of 0.0091 mm and then dried, as described in Example 1 to form an ink receptor medium. When the ink receptor medium was imaged using an HP Designjet 2500cp thermal inkjet printer, the ink receptor medium provided a very high density, high quality, instantaneously dry image having a significant amount of ink beading and coalescence.

Composition-IV

Ingredient	Parts
Aluminum Sulfate, 14 H_2O (Inorganic Salt)	3
Dihexylsulfosuccinate-Na Salt (Surfactant)	6
PVP/AA (75:25) (Binder)	2
Isopropyl Alcohol	25
De-ionized Water	64

Example 15 (Comparative)

A 24 inch x 16 inch (61 x 41 cm) piece of TESLIN film was flood coated with Composition-IV over one-half of its surface (as described in Example 1) and the remaining half of the surface was left uncoated. The coated substrate was dried as described above to form an ink receptor medium. The dry substrate was imaged using an HP Designjet 2500cp thermal inkjet printer to obtain a very high density image as described above. The image on the coated portion of the image provided a higher density image than did the un-coated surface. The imaged substrate was laminated onto an aluminum board/backing (poster board). The image was then subjected to the wash-fastness test. Both images were washed away to an extent of 75-85 percent.

Example 16

The Procedure of Example 15 was repeated except that sulfophthalic acid (9.6 parts) was added to 93.4 parts Composition-IV. The printed image had a similar image quality as that of the image of Example 15. However, only about 20-30 percent of the image color was lost in the wash-fastness test. This marked improvement illustrates the advantages of using organometallic salts according to the invention.

Example 17

The procedure of Example 15 was repeated except that phthalic acid (4.5 parts, at aluminum-sulfate:phthalic acid molar ratio of 1:3) was added to 95.5 parts Composition-IV. The printed image had a similar image quality as that of the image of Example 15. However, only about 10-20 percent of the image color was lost in the wash-fastness test. This marked improvement illustrates the advantages of using organometallic salts according to the invention.

Example 18

The procedure of Example 15 was repeated except that 1,2,4-benzenetricarboxylic acid (5.7 percent, at aluminum sulfate:tricarboxylic acid molar ratio of 1:3) was added to 94.3 parts of Composition-IV. Following the wash-fastness test, only about 20-30 percent of the image color was lost and some feathering occurred. This improvement illustrates the advantages of using organometallic salts according to the present invention.

Example 19

Composition-I was flood coated onto a TEXWRITE MP-10 silica filled substrate (silica-filled HDPE film from Texwipe Co.) and then dried as described in Example 1 to form an ink receptor medium. The substrate was imaged as described in Example 1, providing an image having similar image quality as the image of Example 1. About 5-7 percent of the image was washed away in the wash-fastness test test.

Example 20

The procedure of Example 1 was repeated except a piece of TESLIN film was used as the substrate. The image quality and wash-fastness of the sample was the same as that of Example 1.

Example 21

The procedure of Example 8 was repeated except that a piece of TESLIN film was used as the substrate. The image quality and wash-fastness of the sample was the same as that of Example 8.

The invention is not limited to the above embodiments.

What is claimed is:

1. An ink receptor medium comprising:

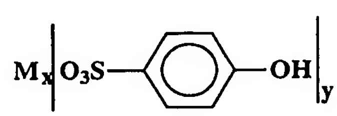
a silica-filled microporous substrate having a silica surface; and

an organometallic multivalent metal salt on the silica surface of the silica-filled microporous substrate.

2. The ink receptor medium of claim 1 further comprising a surfactant on the silica surface of the silica-filled microporous substrate.

3. The ink receptor medium of claim 2 further comprising a binder on the silica surface of the silica-filled microporous substrate.

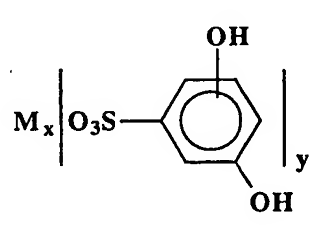
4. The ink receptor medium of claim 1 wherein the organometallic multivalent salt is selected from the group consisting of metal sulfocarbolates having the formula:



wherein

when M is Cu, Mg, Zn, Ca, or Co, the ratio of x:y is 1:2; and when M is Al, Ga, B, then the ratio of x:y is 1:3 or 2:3;

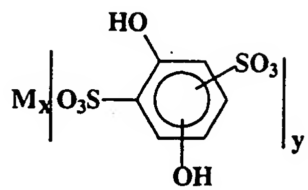
metal hydroquinonesulfonates having the formula:



wherein

when M is Cu, Mg, Zn, Ca, or Co, the ratio of x:y is 1:2 or 2:2; and when M is Al, Ga, B, Ti, Zr, or Hf, the ratio of x:y is 1:3, 2:3 or 2:2;

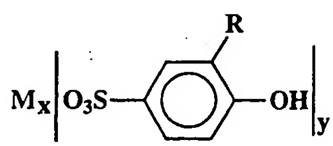
metal dihydroxybenzenedisulfonates having the formula:



wherein

when M is Cu, Mg, Zn, Ca, or Co, the ratio of x:y is 1:2 or 2:2; and when M is Al, Ga, B, Ti, Zr, or Hf, the ratio of x:y is 1:1, 1:3, 2:2, or 4:3;

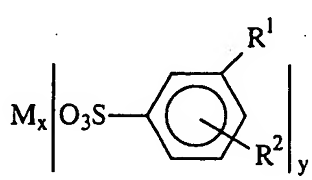
metal sulfosalicylates having the formula:



wherein

when M is Cu, Mg, Zn, Ca, or Co, the ratio of x:y is 1:2 or 1:1; when M is Al, Ga, B, Ti, Zr, or Hf, the ratio of x:y is 1:3, 2:3, or 3:3; and R is –COOH (Li, Na, or K);

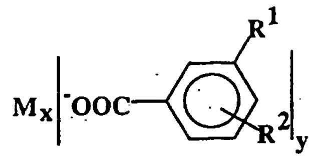
metal sulfophthalates having the formula:



wherein

when M is Cu, Mg, Zn, Ca, or Co, the ratio of x:y is 3:2, 2:2 or 1:1; when M is Al, Ga, B, Ti, Zr, or Hf, the ratio of x:y is 1:3, 2:2, or 2:3; R^1 is H or –COOH (Li, Na, or K); and R^2 is –COOH (Li, Na, or K); and

metal carboxylates having the formula:



wherein

when M is Cu, Mg, Zn, Ca or Co, then the ratio of x:y is 1:1, 2:2, or 3:2; when M is Al, Ga, B, Ti, Zr, or Hf, then the ratio of x:y is 1:3, 2:2, or 2:3; R^1 is H or COOH (Li, Na, or K) and R^2 is COOH ((Li, Na, or K).

5. The ink receptor medium of claim 1 wherein the organometallic multivalent metal salt is magnesium sulfophthalate, copper sulfophthalate, zirconium sulfophthalate, zirconium phthalate, aluminum sulfophthalate, aluminum sulfoisophthalate, or combinations thereof.

6. The ink receptor medium of claim 2 wherein the surfactant is non-ionic, cationic, anionic, or a combination of anionic and non-ionic surfactants.

7. The ink receptor medium of claim 2 wherein the surfactant is anionic.

8. The ink receptor of claim 6 wherein the anionic surfactant is dihexylsulfosuccinate-sodium salt.

9. The ink receptor medium of claim 3 wherein the binder is selected from the group consisting of acrylic emulsions, styrene-acrylic emulsions, polyvinyl alcohol, polyvinyl alcohol/acrylic acid combinations, and combinations thereof.

10. The ink receptor medium of claim 1 wherein the silica-filled microporous substrate has pores that have pores sizes of 0.02 to 0.5 micrometers.

11. An ink receiving medium/ink set comprising a silica-filled microporous substrate having a silica surface and an organometallic multivalent salt on the silica surface of said substrate; and an ink that contains pigment colorants.

12. The ink receiving medium/ink set of claim 11 wherein the silica surface of the microporous substrate further comprises a surfactant thereon.

13. The ink receiving medium/ink set of claim 12 wherein the organometallic multivalent metal salt is magnesium sulfophthalate, copper sulfophthalate, zirconium sulfophthalate, zirconium phthalate, aluminum sulfophthalate, aluminum sulfoisophthalate, or combinations thereof.

14. The ink receiving medium/ink set of claim 13 wherein the surfactant is an anionic surfactant.

15. An ink receptor medium intermediate comprising:
an aqueous composition comprising an organometallic salt on a silica surface of a silica-filled microporous substrate.

16. The ink receptor intermediate of claim 15 further comprising a surfactant.

17. The ink receptor intermediate of claim 16 further comprising an organic solvent.

18. The ink receptor intermediate according to claim 17 further comprising organic binder.

19. The ink receptor intermediate according to claim 16 wherein the organometallic multivalent salt is magnesium sulfophthalate, copper sulfophthalate, zirconium sulfophthalate, zirconium phthalate, aluminum sulfophthalate, aluminum sulfoisophthalate, or combinations thereof.

20. The ink receptor intermediate of claim 19 wherein the surfactant is an anionic surfactant.

21. The ink receptor medium of claim 1 having an image on the silica surface.

22. The imaged ink receptor medium of claim 21 wherein the image is an ink jet image.

23. The imaged ink receptor medium of claim 21 wherein the image is wash-fast.

24. A method of imaging an ink receptor comprising the step of applying ink to the surface of an ink receptor medium using an ink jet printer head, the ink receptor medium comprising a silica-filled microporous substrate having a silica surface; and an organometallic multivalent metal salt on the silica surface of the silica-filled microporous substrate.

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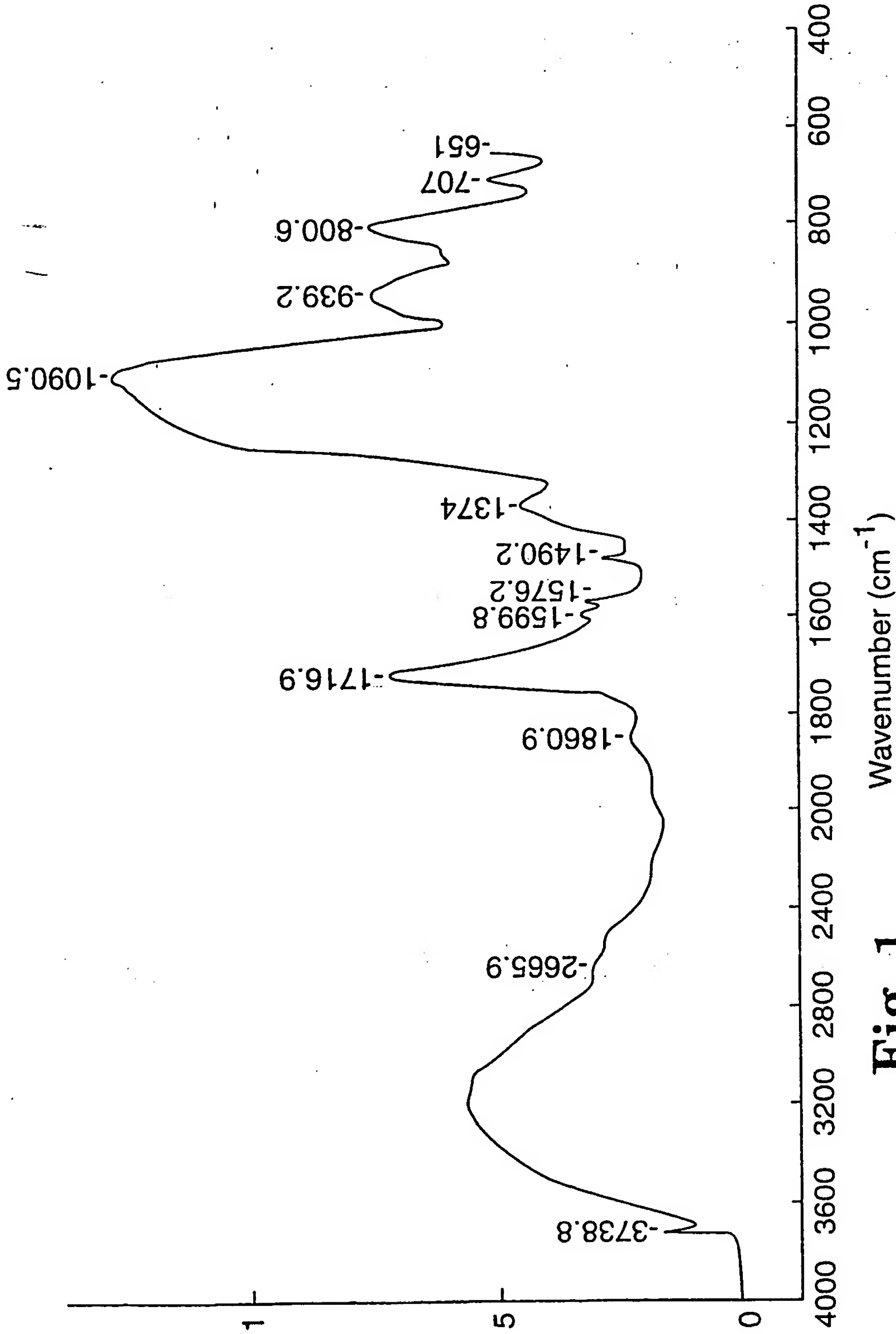

Fig. 1

INTERNATIONAL SEARCH REPORT

Intern nal Application No
PCT/US 00/08156

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B41M5/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B41M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 897 808 A (XEROX CORP) 24 February 1999 (1999-02-24) paragraph [0025] page 3, line 44 claim 1 paragraph [0019] -----	1,3,4, 9-11, 21-24

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 July 2000	09. 08. 2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Martins Lopes, L

2

INTERNATIONAL SEARCH REPORT	International application No. PCT/US 00/08156

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.: 15-20
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:

It is not possible, even after consulting the description which uses the same wording (page 2, lines 26-28), to determine clearly the object of independent claim 15. Is it in the form of a composition or in the form of a ink-receptor medium, or any other form ?

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 15-20

It is not possible, even after consulting the description which uses the same wording (page 2, lines 26-28), to determine clearly the object of independent claim 15. Is it in the form of a composition or in the form of a ink-receptor medium, or any other form ?

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. ,nal Application No
PCT/US 00/08156

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0897808 A	24-02-1999	JP 11165461 A	22-06-1999